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Creation of acid–base bifunctional catalysis for efficient C–C coupling reactions by amines immobilization on SiO_2, silica-alumina, and nano-H-ZSM-5☆

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ABSTRACT

Silica-supported amines (SiO_2-NR_2) were found to be excellent heterogeneous catalysts for various organic C–C coupling reactions, namely cyanation, Michael reaction, and nitro–aldol reaction. A wide variety of substrates, such as aromatic, heteroaromatic, aliphatic, and cyclic carbonyl compounds, can be efficiently converted into the corresponding cyano-*O*-ethoxycarbonylation products. The SiO_2-NR_2 also promoted Michael reaction of ethyl cyanoacetae with cyclohexen-1-one and nitro–aldol reaction of nitromethane with benzaldehyde. These reactions proceeded on the catalyst surfaces, and the SiO_2-NR_2 catalysts were able to be reused without any significant loss of catalytic performance. Notably, these reactions were hard to occur either with amines alone or on the SiO_2 alone, which indicates a dual activation mechanism of basic amine group and surface silanol. In addition, amines immobilized on more acidic support of silica-alumina showed higher catalytic performances than that of the SiO_2-NR_2.

1. Introduction

Heterogeneous catalysts have inherent advantages of being operationally simple as well as enabling highly efficient organic syntheses owing to their unique catalytic abilities [1]. Recently, most attempts have focused on the anchoring of soluble active species on an insoluble matrix via covalent bonding; however these hybrid catalysts often meet the disadvantages, such as (i) inferior activities as compared to homogeneous precursors, (ii) necessity of tedious preparation methods, and (iii) leaching of active species. To overcome these problems, a new concept for the design of hybrid heterogeneous catalysts has been considerably desired.

Much attention has been paid to the creation of multifunction in a single reactor, which allows combination of several reactions or work in a cooperative manner to improve the characteristics in a single reaction, such as rates and selectivities. Not only bifunctional catalysis of different active centers on separate solid surfaces [2,3], but also a cooperative effect of two functions coexisting on a solid surface are also attractive protocol for creation of novel catalysis. Especially, acid–base bifunctional catalyst plays a pivotal role in double activation of electrophiles and nucleophiles, respectively [4]. Recently, heterogeneous catalysts having acid–base bifunctional surfaces have been reported [5]. Cooperative acid–base catalysis of amine and silanol group in silica matrix for Knoevenagel condensation and nitro–aldol reaction was reported by Katz and co-workers [5c]. Lin and co-workers reported silica-supported hydrogen-bonding urea and amine bifunctional catalysts for aldol reaction and cyanosilylation [5a]. Davis and co-workers also demonstrated a multifunctional heterogeneous catalyst of SBA-15-containing amine and sulfonic acid for aldol reaction [5b]. These bifunctional catalysts possessed higher activity than catalysts with either acid or base function.

In this context, we demonstrate a silica-supported tertiary amine catalyst (SiO_2-NEt_2) as an acid–base bifunctional catalyst for various organic transformations, such as cyano-*O*-ethoxycarbonylation and Michael reaction (Scheme 1, Eqs. (1) and (2)). Additionally, a silica-supported primary amine catalyst was also found to be a good catalyst for nitro–aldol reaction (Eq. (3)) [6]. The advantages of these catalyst systems were (i) easy preparation of the catalysts by simple silane-coupling reactions, (ii) high catalytic activity and selectivity, and (iii) reusable heterogeneous catalysis. The results of catalytic performances in the case of more acidic supports of nano-H-ZSM-5 zeolite and silica-alumina for amine immobiizeation were also mentioned.

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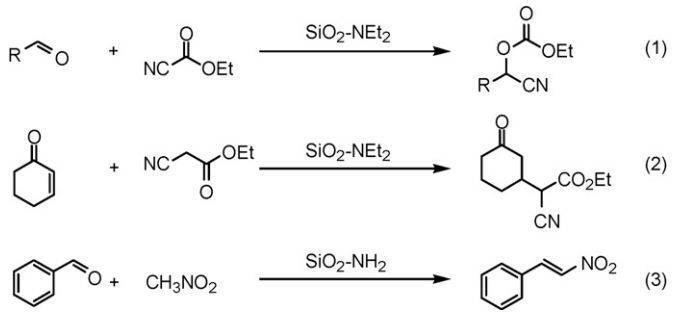


Scheme 1. SiO_2-NR_2-catalyzed reactions.

2. Experimental

2.1. General

^1H and ^{13}C NMR spectra were obtained on JNM-AL400 spectrometer at 400 MHz in $CDCl_3$ with TMS as an internal standard. Solid state ^{13}C and ^{29}Si MAS NMR spectra (MAS rate = 4 kHz) were recorded with a Chemagnetics CMX-300 spectrometer operating at 75.5 and 59.7 MHz, respectively. Repetition times were 15 s (^{13}C) and 20 s (^{29}Si). Hexamethylbenzene (^{13}C: 17.17 and 176.46 ppm) and TMS (^{29}Si: 0 ppm) were used as external standards for the calibration of chemical shifts. Analytical GLC and GLC-Mass were performed by Shimadzu GC-8A PF with flame ionization detector equipped with Silicon SE-30 column. Unless otherwise noted, materials were purchased from Wako Pure Chemicals, Tokyo Kasei Co., Nacalai tesque, and Aldrich Inc. and were used after appropriate purification. Aerosil® 300 was used as silica. The silica-alumina (SA, SiO_2, 66.5; Al_2O_3, 25.1%, 380 m^2/g) was purchased from Nikki Chemical Co.

2.2. Preparation of catalysts

2.2.1. SiO_2-NR_2

Silica (surface area 300 $m^2\ g^{-1}$, 1.0 g) was added to 20 mL of a toluene solution of 3-(diethylamino)propyltrimethoxysilane (2 mmol) and refluxed for 24 h. Then the toluene was removed by filtration and the obtained functionalized silica was washed with dichloromethane, followed by drying under vacuum, which affords the SiO_2-NEt_2. In the case of the SiO_2-NH_2 catalyst, 3-aminopropyltriethoxysilane was used as a precursor under similar reaction conditions. Elemental analysis results were as follows: SiO_2-NEt_2, C: 6.58, H: 1.42, N: 0.99; SiO_2-NH_2, C: 3.57, H: 0.91, N: 1.04, nano-H-ZSM-5-NEt_2, C: 10.94, H: 2.4, N: 1.23.

2.3. Typical procedures for organic reactions using the heterogeneous catalysts

2.3.1. Cyano-O-ethoxycarbonylation using the SiO_2-NEt_2

Into a pyrex glass reactor were placed the SiO_2-NEt_2 (0.05 g, 0.035 mmol), toluene (1 mL), ethyl cyanoformate (1.0 mmol), and benzaldehyde (0.5 mmol). The resulting mixture was vigorously stirred at room temperature under Ar. After 1 h, the catalyst was separated by filtration and the GC analysis of the filtrate showed 99% conversion of benzaldehyde and 95% yield of the addition product. The recovered catalyst was washed with toluene, dried in vacuum, and reused under the same reaction conditions: 99% conversion and 95% yield of the product were obtained in the reuse experiment.

2.3.2. Michael reaction using the SiO_2-NEt_2

Into a pyrex glass reactor were placed the SiO_2-NEt_2 (0.05 g, 0.0035 mmol), toluene (1 mL), ethyl cyanoacetate (0.5 mmol), and 2-cyclohexen-1-one (1.0 mmol). The resulting mixture was vigorously stirred at 60 °C under Ar. After 6 h, the catalyst was separated by filtration and the GC analysis of the filtrate showed a 36% yield of addition product.

2.3.3. Nitro–aldol reaction using the SiO_2-NH_2

Into a pyrex glass reactor were placed the SiO_2-NH_2 (0.015 mmol of amine), nitromethane (2 mL), and benzaldehyde (5.0 mmol). The resulting mixture was vigorously stirred at 100 °C. After 6 h, the catalyst was separated by filtration and GC analysis of the filtrate showed 37% yield of β-nitrostyrene product.

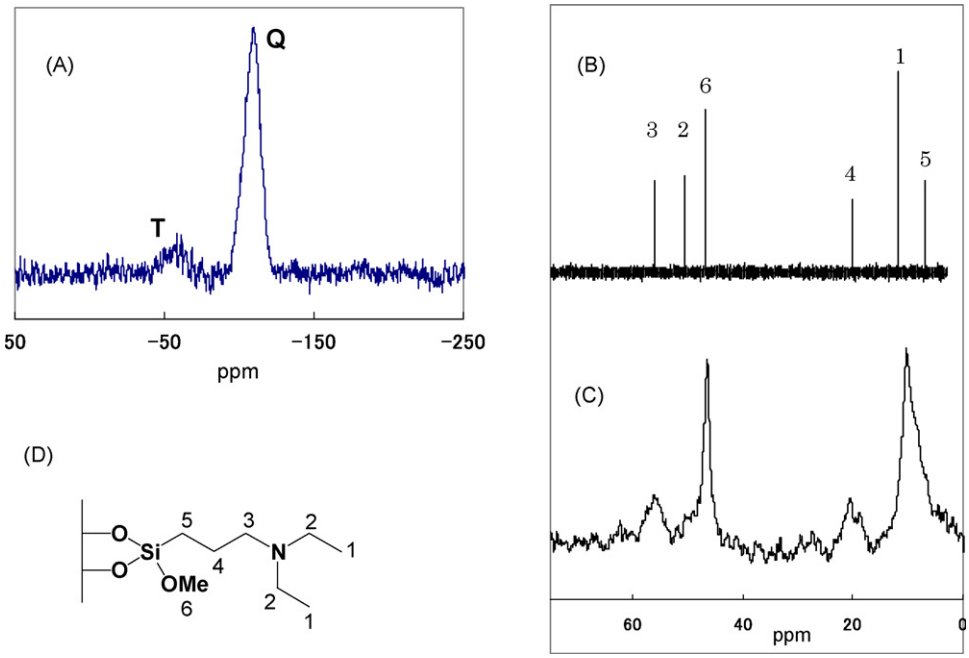


Fig. 1. (A) ^{29}Si MAS NMR of SiO_2-NEt_2, (B) ^{13}C NMR of 3-(diethylamino)propyltrimethoxy- silane, (C) ^{13}C CP MAS NMR of SiO_2-NEt_2, and (D) Proposed surface structure of SiO_2-NEt_2.

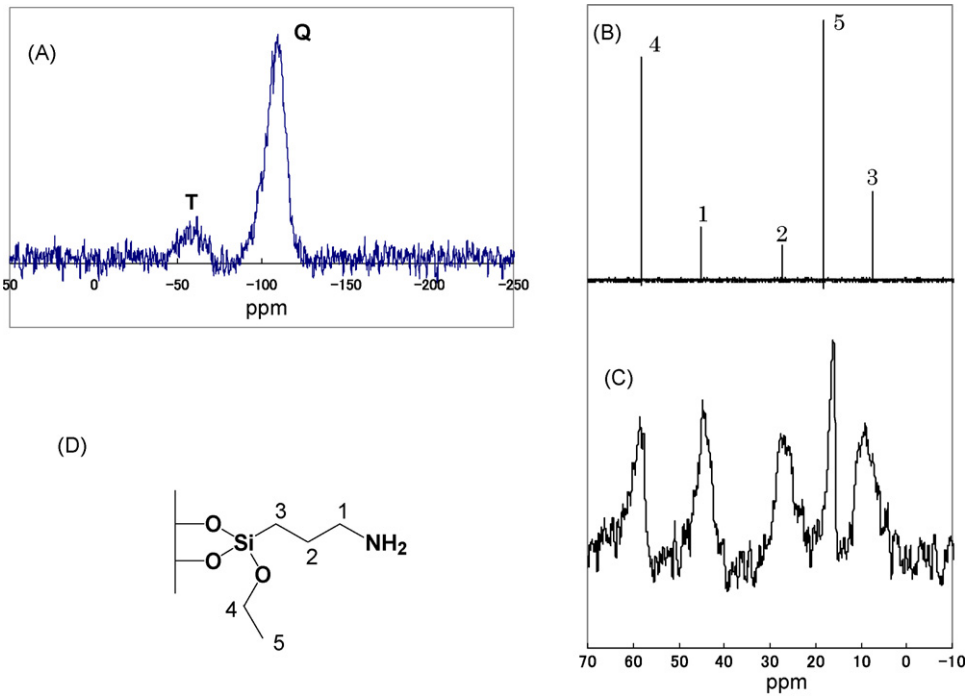


Fig. 2. (A) ^{29}Si MAS NMR of SiO_2-NH_2, (B) ^{13}C NMR of aminopropyltriethoxysilane, (C) ^{13}C CP MAS NMR of SiO_2-NH_2, and (D) proposed surface structure of SiO_2-NH_2.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. SiO_2-NEt_2

The elemental analysis of the SiO_2-NEt_2 revealed that the C/N ratio of the SA-NEt_2 was 7.8, and the amount of the amine group was 1.4 molecules/nm^2. Solid state ^{29}Si MAS NMR for immobilized Si atoms exhibited chemical shifts due to the formation of Si–O bonds with the silica surface (Fig. 1A). The presence of the intact 3-(diethylamino)propyl and methoxy groups was indicated by the solid state ^{13}C MAS NMR spectra (Fig. 1C). Conclusively, a proposed structure of the SiO_2-NEt_2 catalyst is illustrated in Fig. 1D.

3.1.2. SiO_2-NH_2

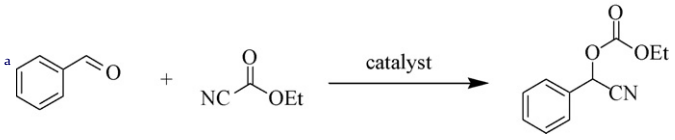
The elemental analysis of the SiO_2-NH_2 revealed that the C/N ratio of the SA-NH_2 was 4.0, and the amount of the amine group was 1.5 molecules/nm^2. As similar to the SiO_2-NEt_2, solid state ^{29}Si and ^{13}C MAS NMR indicated that immobilized Si atoms formed Si–O bonds with the silica surface (Fig. 2A), and the intact of aminopropyl function (Fig. 2C). A proposed structure of the SiO_2-NEt_2 catalyst is illustrated in Fig. 2D.

3.2. Cyano-O-ethoxycarbonylation of carbonyl compounds using the SiO_2-NEt_2

Cyanohydrins are one of the most important synthetic building blocks. Recently, one-pot catalytic cyanation-*O*-protection reaction with a robust protecting group has been investigated [7] because of the instability of cyanohydrins and highly toxicity of traditional cyanide sources, such as HCN and Me_3SiCN. Cyano-ethoxycarbonylation of benzaldehyde with ethyl cyanoformate was carried out using various heterogeneous and homogeneous catalysts as shown in Table 1. Remarkably, the SiO_2-NEt_3 was found to be an excellent catalyst for the reaction of ethyl cyanoformate with benzaldheyde, affording cyanation product (entry 1), while the reaction scarcely proceeded using either parent SiO_2 (entry 4), the precursor of 3-(diethylamino)propyl trimethoxysilane (entry 5), or triethylamine (entry 6) as a catalyst. Amine-immobilized nano-H-ZSM-5 also showed a catalytic activity, affording moderate yield of the product (entry 3). After the SiO_2-NEt_2-catalyzed reaction, the solid catalyst was able to be recovered from the reaction mixture by simple filtration, and reused with retention of its high catalytic activity and selectivity (entry 2). As shown in Fig. 3, no reaction was observed after the removal of the SiO_2-NEt_2 catalyst. Furthermore, it was confirmed by ^{1}H NMR analysis that no alkylamine compounds were present in the filtrate. These facts rule out any contribution to the observed catalysis from amine that leaches into the reaction solution. Thus, the observed catalysis is obviously heterogeneous.

The SiO_2-NEt_2-catalyzed cyano-ethoxycarbonylation was extended to other carbonyl compounds as shown in Table 2. A heteroaromatic aldehyde of 4-formylpyridine reacted with ethyl

Table 1
Cyano-*O*-ethoxycarbonylation using various catalysts



Entry	Catalyst	Coversion of benzaldehyde (%)[b]
1	SiO_2-NEt_2	>99
2	SiO_2-NEt_2 (2nd use)	>99
3	Nano-H-ZSM-5-NEt_2	52
4[c]	SiO_2	N.R.
5	$(MeO)_3Si$⌇⌇NEt_2	8
6	Et_3N	3
7	None	N.R.

N.R. = no reaction.
[a] Benzaldehyde (0.5 mmol), ethyl cyanoformate (1.0 mmol), catalyst (0.035 mmol of amine), toluene (1 mL), 1 h, room temp.
[b] Determined by GC.
[c] 0.05 g of SiO_2 was used.

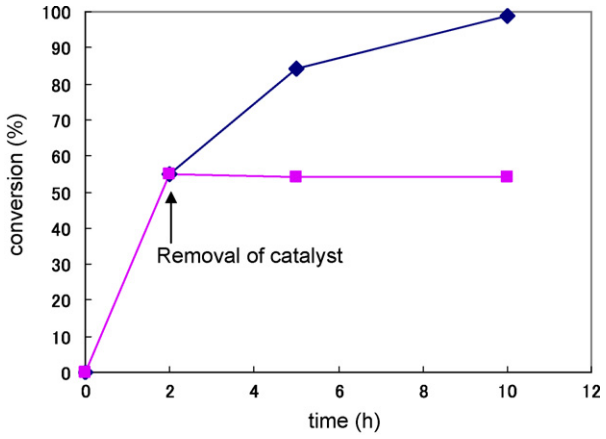
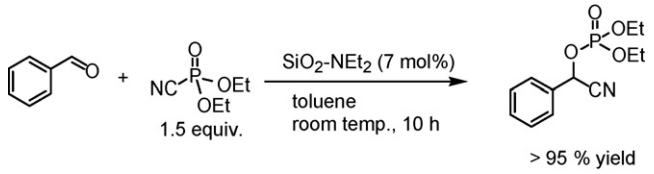


Fig. 3. Effect of removal of SiO_2-NEt_2 on the cyano-*O*-ethoxycarbonylation of benzaldehyde. Without removal (◆); an arrow indicates the removal of SiO_2-NEt_2 (■). Reaction conditions: benzaldehyde (0.5 mmol), ethyl cyanoformate (1.0 mmol), catalyst (0.035 mmo of amine), toluene (5 mL), room temp.

cyanoformate to give the corresponding product in an excellent yield (entry 2). Reactions of cinnamaldehyde proceeded smoothly, suppressing the 1,4-conjugate addition reaction (entry 3). An aliphatic aldehyde also worked well as a good substrate in the SiO_2-NEt_2-catalyzed reaction, affording the 94% yield of the cyanation product (entry 4). Interestingly, the reaction of less reactive cyclohexanone also proceeded with good performance in this SiO_2-NEt_2 catalyst system (entries 5). Notably, the cyano-*O*-phosphination of benzaldehyde also proceeded in the presence of the SiO_2-NEt_2 catalyst (Scheme 2).

3.3. Michael reaction of ethyl cyanoacetate with 2-cyclohexen-1-one using the SiO_2-NEt_2

Michael reaction of ethyl cyanoacetate to 2-cyclohexen-1-one using various heterogeneous and homogeneous catalysts was examined, as shown in Table 3. The SiO_2-NEt_2 possessed highest catalytic activity to afford α-cyano-3-oxo-cyclohexaneacetic acid ethyl ester (entry 1), while the reaction rate significantly decreased



Scheme 2. Cyano-*O*-phosphination catalyzed by SiO_2-NEt_2.

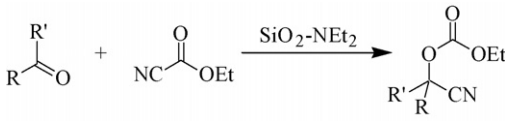
using either amine precursor of 3-(diethylamino)propyltrimethoxysilane (entry 2), triethylamine (entry 3), or silica (entry 4) as a catalyst. Notably, the reaction using physical mixture of triethylamine and silica afforded the corresponding product (entry 5); however the catalytic activity was lower than that of the immobilized SiO_2-NEt_2 catalyst. In general, conjugate addition of nitrile compounds to α,β-unsaturated ketones needs strong base catalyst, such as sodium alkoxide, which faced the difficulties for handling due to moisture sensitivity and highly toxicity [8]. The use of the simple and stable alkyl amine as a heterogeneous catalyst makes the environmentally friendly organic synthesis a reality (Table 3).

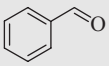
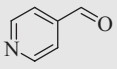
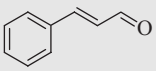
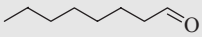
3.4. Nitro–aldol reaction using the SiO_2-NH_2 catalyst

The high performance of the SiO_2-supported amine catalysts was highlighted by the nitrostyrene synthesis. The nitro–aldol reaction of benzaldehyde with nitromethane using heterogeneous and homogeneous primary amine catalysts was examined as shown in Scheme 3. The reaction in the presence of the SiO_2-NH_2 gave the turn over number (TON) of 124 and turn over frequency (TOF) of 21 h^{-1} for the nitro–aldol reaction three times larger than that of a homogeneous primary amine, *n*-hexylamine.

Because of a decrease in the reaction rate by the treatment of free Si–OH groups on the SiO_2-NEt_2 surface with hexamethyldisiloxane, these high catalytic activities of the SiO_2-NR_2 may derive from the acidity of the surface silanol group. A proposed reaction pathway involves the dual activation of donors, such as nitriles and nitromethane, and acceptors, carbonyl compounds, at the amine base and the acidic Si–OH site on the silica surface, respectively

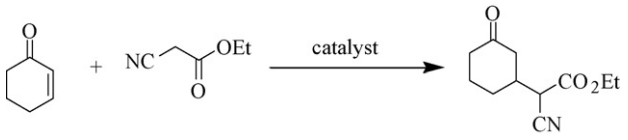
Table 2
Cyano-*O*-ethoxycarbonylation using the SiO_2-NEt_2 catalyst[a]



Entry	Carbonyl compounds	Time (h)	Conversion (%)[b]	Yield (%)[b]
1		1	>99	98
2		1	>99	87
3		5	>99	96
4		3	94	94
5		48	92	86

[a] Carbonyl compounds (0.5 mmol), ethyl cyanoformate (0.6 mmol), SiO_2-NEt_2 (0.05 g, 0.035 mmo of amine), toluene (1 mL), room temp.
[b] Determined by GC.

Table 3
Michael addition of ethyl cyanoacetate with 2-cyclohexen-1-one using various catalysts[a]



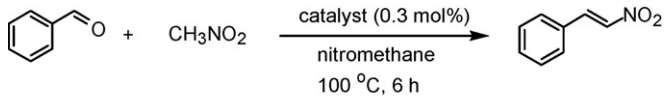
Entry	Catalyst	Initial rate (10^{-2} mmol/h)[b]
1	SiO_2-NEt_2	6.0
2	$(MeO)_3Si$⁄⁄NEt_2	0.50
3	Et_3N	0.83
4[c]	SiO_2	N.R.
5[c]	Et_3N + SiO_2 (physical mixture)	4.5
6	None	N.R.

N.R. = no reaction.
[a] 2-Cyclohexen-1-one (1.0 mmol), ethyl cyanoacetate (1.0 mmol), catalyst (0.035 mmol of amine), toluene (1 mL), 80 °C.
[b] Determined by GC.
[c] 0.05 g of SiO_2 was used.

(Scheme 4). The further investigation of the supported-amine catalysis is now under progress.

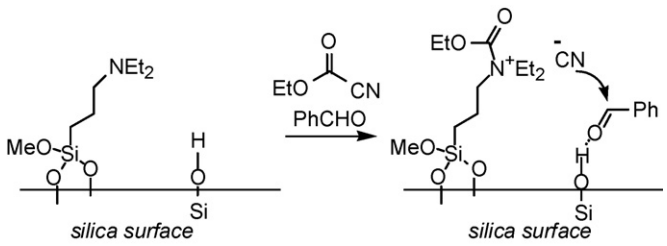
3.5. Silica-alumina-supported amine catalysts for carbon–carbon bond-forming reactions

From SiO_2-NR_2-catalyzed reaction results, it can be said that the surface acid site acts as a pivotal role for the acceleration of catalytic reaction rates. We envisaged that the use of more acidic support would significantly improve catalytic activity, and silica-alumina (SA) possessing strong Brønsted acid site was examined as a support of tertiary and primary amines [9]. SA-supported tertiary amine and primary amine catalysts (SA-NEt_2 and SA-NH_2) were prepared by similar procedures to the SiO_2-NEt_2 and SiO_2-NH_2, respectively. The elemental analyses of the SA-NEt_2 and SA-NH_2 determined that C: 8.40, H: 2.16, and N: 1.27 wt% (SA-NEt_2), and C: 6.41, H: 1.99, N: 1.57 wt% (SA-NH_2). The presence of intact amine groups in the SA-NEt_2 and SA-NH_2 was indicated by the solid-state ^{13}C CP/MAS NMR spectra. Solid-state ^{29}Si MAS NMR revealed that



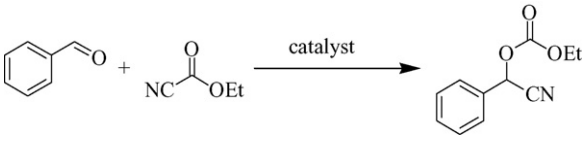
catalyst	TON	TOF (h^{-1})
SiO_2-NH_2	124	21
n-$C_6H_{13}NH_2$	43	7.2
SiO_2	N.R.	N.R.

Scheme 3. Nitro–aldol reaction of nitromethane with benzaldehyde.



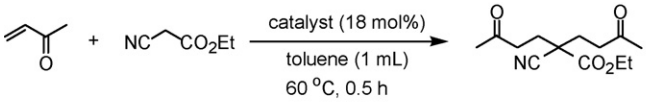
Scheme 4. Proposed dual activation pathway.

Table 4
Comparison of catalytic activity for cyano-*O*-ethoxycarbonylation with a low substrate concentration[a]



Entry	Catalyst	Yield (%)[b]
1	SA-NEt_2	95
2	SiO_2-NEt_2	17
3	Al_2O_3-NEt_2	16
4	SA + triethylamine	70
5	Triethylamine	1
6	SA	<1

[a] Benzaldehyde (0.5 mmol), ethyl cyanoformate (1.0 mmol), catalyst (0.035 mmol of amine), toluene (5 mL), 1 h, room temp.
[b] Determined by GC.

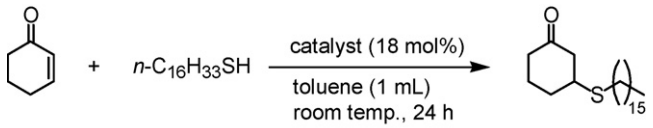


catalyst, yield (%); **SA-NEt_2, 90%**; SiO_2-NEt_2, 43%; NEt_3, <1%

Scheme 5. Catalysis of SA-NEt_2 for Michael reaction of MVK.

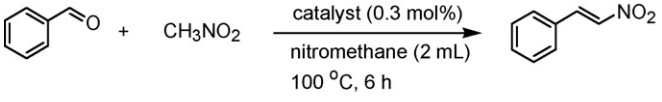
immobilized Si atoms exhibited chemical shifts owing to the generation of Si–O bonds with the SA surface.

The catalytic activity of the SA-NEt_2 for the cyano-ethoxycarbonylation between ethyl cyanoformate and benzaldehyde was compared with that of the another amine catalysts, such as SiO_2-NEt_2, under lower concentrations of substrates and catalysts than those of Table 1. As shown in Table 4, the SA-NEt_2 showed a significantly higher performance (entry 1) than that of the SiO_2-NEt_2 (entry 2). Michael reaction of ethyl cyanoacetate with methyl vinyl ketone was also examined with use of amine catalysts (Scheme 5). Remarkably, a 90% yield of double alkylated product was obtained in the case of the SA-NEt_2 catalyst, while the SiO_2-NEt_2-catalyzed reaction afforded only 43% yield of the product under same reaction conditions. The SA-NEt_2 catalyst is also active for Michael reaction of a thiol compound for C–S bond-formation, which did not promoted by homogeneous amine (Scheme 6). The SA-NH_2 was also found to be an excellent catalyst for nitro–aldol reaction of nitromethane with benzaldehyde, affording quantitative yield of 2-nitrostyrene (Scheme 7). Strong acid site on SA



catalyst, yield (%); **SA-NEt_2, 90%**; NEt_3, 4%; SA, 1%

Scheme 6. Catalysis of SA-NEt_2 for Michael reaction of 1-hexadecanethiol.



catalyst, yield (%); **SA-NH_2, 99%**; SiO_2-NH_2, 37%; *n*-$C_6H_{13}NH_2$, 13%

Scheme 7. Catalysis of SA-NH_2 for nitro–aldol reaction.

surface can contribute to highly efficient carbon–carbon and carbon–sulfur bond-forming reactions.

4. Conclusion

In this study, we have demonstrated novel heterogeneous acid–base dual functional catalysis for a variety of organic reactions. Unique catalyses of acid–base bifunctional solid surfaces of the silica-supported amine catalysts realized efficient cyanation, Michael reaction, and nitro–aldol reaction. Furthermore, silica-alumina-supported amines were found to be excellent catalysts for above carbon–carbon bond-forming reactions rather than the silica-supported amines. Bifunctional heterogeneous catalysis will allow to develop high-performance environmentally friendly chemical reactions.

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